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Simultaneous removal of organic substances and nitrogen in pilot-scale submerged membrane bioreactors treating digested traditional Chinese medicine wastewater

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ABSTRACT

Influence of dissolved oxygen (DO) concentration on organic substances and nitrogen removal was investigated in pilot-scale submerged membrane bioreactors (SMBRs) degrading digested traditional Chinese medicine (TCM) wastewater. The DO concentration for each SMBR was maintained at 0.6, 1.2, 3.0 and 5.0 mg/L, respectively. Experimental results indicated that DO had an important effect on the chemical oxygen demand (COD) removal and nitrogen conversion. Simultaneous nitrification and denitrification were able to be accomplished in the continuous-aeration SMBRs by controlling ambient DO concentration. It is postulated that, because of the oxygen diffusion limitation, an anoxic micro-zone was formed inside the flocs where the denitrification occurred. From four tested DO levels, the optimal DO concentration favoring COD and total nitrogen removal was found to be 1.2 mg/L. At that DO level, more than 96% COD and 90% total nitrogen were degraded. A model was developed for the SMBR process of degrading the digested TCM effluent, taking into account the biological degradation and membrane separation. The model well fitted the laboratory data, and was able to simulate the removal of COD and nitrogen. It is suggested that the model proposed could reflect and manage the operation of SMBR treating a certain kind of industrial wastewaters.

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1. Introduction

As an innovative and promising wastewater treatment process, submerged membrane bioreactor (SMBR) process has been widely applied in the organic removal of domestic wastewater (Bailey et al., 1994; Xing et al., 1998; Ren et al., 2005a,b; Chu et al., 2006) and industrial wastewater (Seo et al., 1997; Ren et al., 2005a,b) in recent decades. The SMBR allows a higher level of biomass to retain and slow-growing microorganisms to enrich, such as nitrifiers which improve biochemical reaction rates and system performance as well as nutrients removal (Silva et al., 1998). Most studies on SMBR processes were focused on the feasibility of wastewaters treatment, optimization of operating conditions and system stability (Hibiya et al., 2003; Chu et al., 2006; Holakoo et al., 2007).

Although simultaneous nitrification and denitrification (SND) had been noted in the SMBR process, relevant studies remain limited. Many factors, for example hydraulic retention time (HRT) (Jeff et al., 2000) and sludge retention time (SRT) (Sun et al., 2007), might affect SND process. As nitrogen removal requires both aerobic and anoxic conditions, ambient dissolved oxygen (DO) concentration is one of the important parameters affecting the SND. In fact, the importance of DO concentration on the SND has been highlighted in the biofilm- and granule-based reactors in which the SND occur as a consequence of DO concentration gradients within microbial biofilms or granules due to diffusion limitation (Zhang et al., 1999; Chu et al., 2006; Holakoo et al., 2007). However, studies on DO effect on nitrogen removal of industrial wastewaters by SMBR processes have not been reported yet. Traditional Chinese medicine (TCM) wastewater is a kind of high-strength organic wastewater, which contains a great variety of pollutants and complicated components (Zhu, 2007). Due to its high chemical oxygen demand (COD), TCM wastewater has been one of the main sources of water pollution in china (Feng, 2005; Shi et al., 2007). Because of its macromolecular composition and easy to foam in aerobic biodegradation, TCM wastewater was generally treated by anaerobic processes (Liu et al., 2007). However, a great amount of pollutants still remain in the digested effluent, and thus a secondary process is commonly required (Li et al., 2006). Applying SMBR process to the digested TCM effluent appears unreported in literature.

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The aim of this work was double. Firstly, an effort was made to investigate the effect of DO concentration on the removal of organic carbon and nitrogen of a digested TCM effluent in pilot-scale SMBRs. The second aim of this work, to simulate and manage the operation of SMBR, consisted of suggesting a model for the SMBR process of degrading the digested TCM effluent, taking into account the biological degradation and membrane separation. This model was inspired by activated sludge model (ASM1) which was developed to model biological treatment for organic carbon removal, nitrification, and denitrification. The simulation model was established by using software program MATLAB which does not appear to have been used in the similar research.

2. Materials and methods

2.1. Wastewater

The effluent of a plant-scale anaerobic digester treating TCM wastewater (Harbin traditional Chinese medicine company, China) was used as the feedstock of the SMBR. Raw TCM wastewater was generated from the processes of washing, distillation, separation, concentration, purification washing, refining, torrefaction, and moulding. Raw TCM wastewater contains a great variety of complicated components, such as glucide, protein, organic acid, amylose, lignin, colophony, mucilage, alkaloid, terpene, hydroxybenzene, long-chain organic acids, innocuity pigment and foliage (Zhu, 2007). Its biochemical oxygen demand (BOD_5) was estimated to be around 10,800 mg/L and COD around 60,000 mg/L, indicating a low biodegrability ($BOD_5/COD < 0.2$). The major characteristics of the digester effluent were as follows: COD, 1259.1–12776.5 mg/L; total nitrogen, 7–25 mg/L; total phosphorus, 5–9 mg/L; and suspended solids (SS), 1000–1600 mg/L.

2.2. Seed sludge

Seed sludge was taken from the aeration tank and sludge collector in Harbin traditional Chinese medicine company. The seed sludge was first enriched with the digester effluent in a batch reactor for one week. After that, a membrane module was added to the bioreactor and the seed sludge was acclimated in such an SMBR with continuous feeding for another one week. After two-week cultivation, the dark sludge became brown and some protozoa, such as rotifer species were observed microscopically. At the same time, reactor sludge concentration (in MLSS) reached 2860 mg/L, and effluent COD was found to be around 150 mg/L.

2.3. MBR system and operation

The schematic diagram of the SMBR system is shown in Fig. 1. The SMBR had a working volume of approximately 3.2 m^3 and was installed with four submerged hollow-fiber PVDF microfiltration (MF) membrane modules (Tianjin Motian Membrane Engineering and Technology Co. Ltd, China). The MF membrane modules are characterized with a pore size of 0.22 μm and an effective surface area of 12.5 m^2. The wastewater was fed continuously by a peristaltic pump. A level controller and an automatic vacuum effluent system were used to control the reactor working volume at a constant value. The automatic vacuum effluent system consisted of vacuum reservoir, vacuum pump, gas–water segregator, level sensor, Pump 2, electron-magnetic valve and power control device. When the vacuum pump worked, a negative-pressure condition was created as gas stored in the vacuum reservoir was pumped out, which would push wastewater to flow into vacuum reservoir from the bioreactor through the membrane module. As the liquid surface in the vacuum reservoir reached 80% of the maximum height, the effluent stored in the reservoir was drained out by Pump 2. The vacuum pump and Pump 2 would alternatively work so that the SMBR effluent was continuously discharged. The sludge was withdrawn continuously by a sludge withdrawing pump to maintain culture SRT. The reactor was operated at a constant temperature of 20 °C.

Two series of runs were conducted to assess the effect of DO (DO run) and model simulation (model run), respectively. In DO run, four identical SMBRs were used and operated at DO concentrations of 0.6, 1.2, 3.0, 5.0 mg/L, respectively. A same HRT of 5.0 h and consistent membrane flux of 12.8 L/(m^2 h) were employed to each reactor throughout the experimental run. Membrane flux in this experiment was kept constant by increasing vacuum value. Sludge concentration was found to stabilize around 2140 mg/L at a consistent SRT of 100 days in each reactor. Three sets of identical SMBRs designated SMBR1, SMBR2 and SMBR3 were used in Model run. HRTs of 8.0, 5.0 and 3.2 h were employed to SMBR1, SMBR2 and SMBR3, corresponding to respective membrane fluxes of 8.0, 12.8 and 20.0 L/(m^2 h). SMBR1 was operated at a SRT of 50 days, and SMBR2 and SMBR3 at a SRT of 100 days. DO was 1.2–3.0 mg/L in three reactors.

2.4. Analytical methods

Measurement of MLSS, MLVSS, COD, BOD_5, ammonium and ammonia nitrogen (S_{NH}), total nitrogen (TN), and nitrate and nitrite nitrogen ($NO_2^- + NO_3^-$; S_{NO}) was performed according to Standard methods (APHA, 1995). Measurements of COD were performed according to the potassium dichromate–ferrous ammonium sulphate method. TN concentration was determined by a TOC analyzer equipped with a total nitrogen-measuring unit (TOC-VcpH, Shimadzu). S_{NH} and S_{NO} were measured following the Kjeldahl distillation method. The mixed liquor and filtrate COD and nitrogen were analyzed and samples were prepared by the following procedures: a certain volume of mixed liquor was taken from the reactor and clarified in a beaker for 30 min. After the clarification, the supernatant COD and nitrogen were measured as the mixed liquor COD (COD_{mix}) and mixed liquor nitrogen. Also, the supernatant was filtrated with a 0.45 μm filter to measure filtrated COD (COD_{fit}) and filtrated nitrogen. DO was measured by a hand-held oxygen meter (COM 381, Shanghai Light Industry Research Institute, China) equipped with a DO probe (COS 381, Shenzhen Futai Instrument Co. Ltd, China). An electro-pressure meter (Hangzhou Eastern Hydraulic Pressure Pneumatic Co., Ltd, China) was used to monitor vacuum values. Membrane effluent flux was measured by a rotor flowmeter (Beijing Master Meter Co., Ltd, China). The kinetic and stoichiometric parameters used in model simulation were determined as described in other models, that is, ASM1, ASM2 and ASM3 (Henze et al., 1987a,b, 1999, 2000; Gujer et al., 1999). Software MATLAB was used to analyze model numerical solutions.

3. Results and discussion

3.1. COD removal

The COD removal at different DO concentrations of 0.6, 1.2, 3.0 and 5.0 mg/L is shown in Fig. 2. Total COD removal rate increased

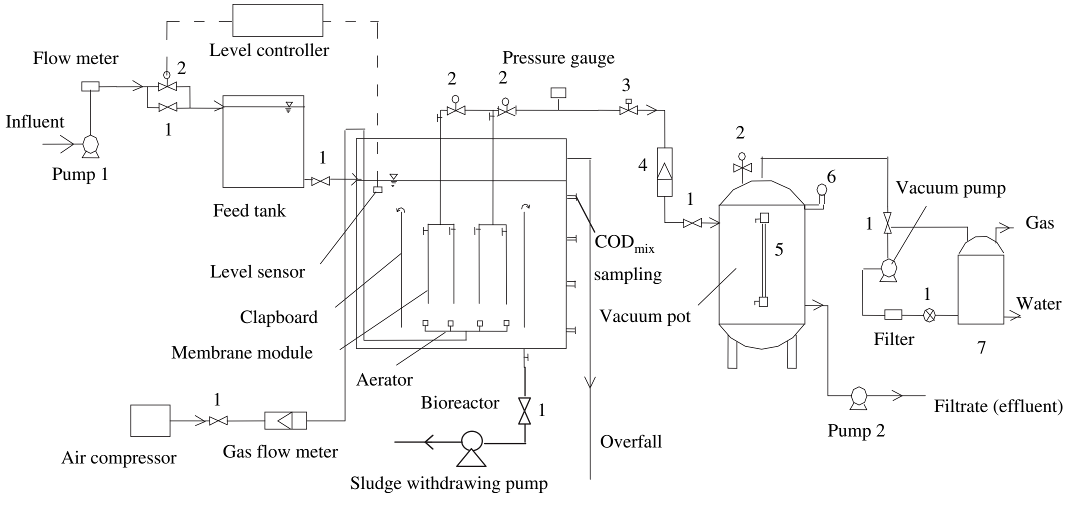

Fig. 1. Schematic diagram of pilot-scale SMBR system.

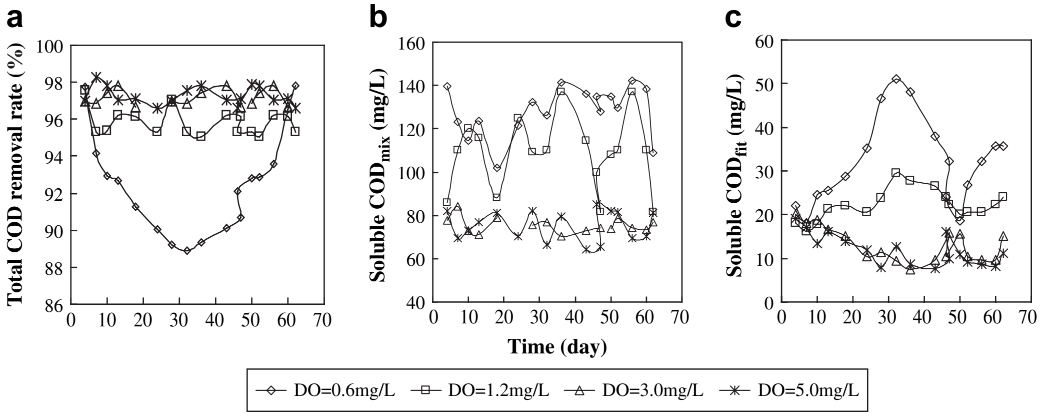

Fig. 2. COD removals at different DO concentrations.

with the increase in DO concentration from 0.6 to 3.0 mg/L, but it did not vary as the DO concentration increased to 5 mg/L. More than 96% COD was removed throughout the study as the DO concentration was controlled in a range of 1.2–5.0 mg/L. At the lowest DO level of 0.6 mg/L, total COD removal rate significantly decreased from 98 to 89% in the first 30 days of operation, but it was resumed to the initial level after another 30 days of operation. Fluctuation of COD removal at a low DO level is presumably attributed to the fact that the activity of bacteria was inhibited as a result of oxygen limitation. As the bacteria well adapted to a low DO environment, more pollutants were degraded and the effluent quality was thus improved.

At higher DO levels of 3 and 5 mg/L, soluble COD_{mix} and COD_{fit} stabilized at around 80 and 10 mg/L, respectively. Reducing DO concentrations to 1.2 and 0.6 mg/L resulted in a dynamic increase in COD_{mix} to a range of 80–140 mg/L. Soluble COD_{fit} also increased with the reduction in DO concentration: soluble COD_{fit} fluctuated between 20 and 50 mg/L at a DO level of 0.6 mg/L, and stabilized at around 20 mg/L at a DO level of 1.2 mg/L. The difference between COD_{mix} and COD_{fit} indicated that a combined removal mechanism functions in the removal of organic pollutants by the SMBR system, that is, microbial degradation and membrane filtration. It is suggested that the DO concentration be controlled at a level no less than 1.2 mg/L to guarantee effluent quality and system efficiency. At that time, the SMBR effluent is able to be reused as it meets the reused water quality standard of less than 30 mg-COD/L ([CJ25.1-89], the Construction Ministry, China).

3.2. Simultaneous nitrification and denitrification

S_{NH} (ammonium and ammonia nitrogen, $NH_4^+ + NH_3$) removal at different DO concentrations is illustrated in Fig. 3. Increasing DO concentration favored nitrification process in the SMBR system. However, S_{NH} conversion was not apparently improved at DO concentrations up to 1.2 mg/L. The mixed liquor S_{NH} and filtrate S_{NH} were detected in the ranges of less than 1.0 and 2.0 mg/L, respectively, resulting in a larger than 95% S_{NH} removal rate at DO levels of 1.2–5.0 mg/L. There was significant influence on S_{NH} conversion as the DO concentration decreased to 0.6 mg/L at which only 40–50% ammonia nitrogen was converted. The activity of S_{NH}-converting bacteria, *Nitrosomonas*, would be greatly inhibited by a low DO level (Wyffel, et al., 2004; Dong et al., 2005), which resulted in an incomplete nitrification. For a purpose of S_{NH} conversion, a minimal DO level of 1.2 mg/L was required by the SMBR system.

Fig. 4 depicts the removal of soluble TN at different DO concentrations. TN removal increased as the DO concentration decreased from 5 to 1.2 mg/L, but it decreased with DO decrease to 0.6 mg/L. About 60% TN was degraded at a DO concentration of 5.0 mg/L, while more than 90% TN was consumed at a DO concentration of 1.2 mg/L. As the optimal removal rate of TN was achieved, mixed liquor and filtrate TN concentrations were found to be less than 4 and 2 mg/L, respectively. As shown in Fig. 5, S_{NO} (nitrate and nitrite nitrogen, $NO_2^- + NO_3^-$) concentration increased with the DO concentration. Almost no S_{NO} was accumulated in the

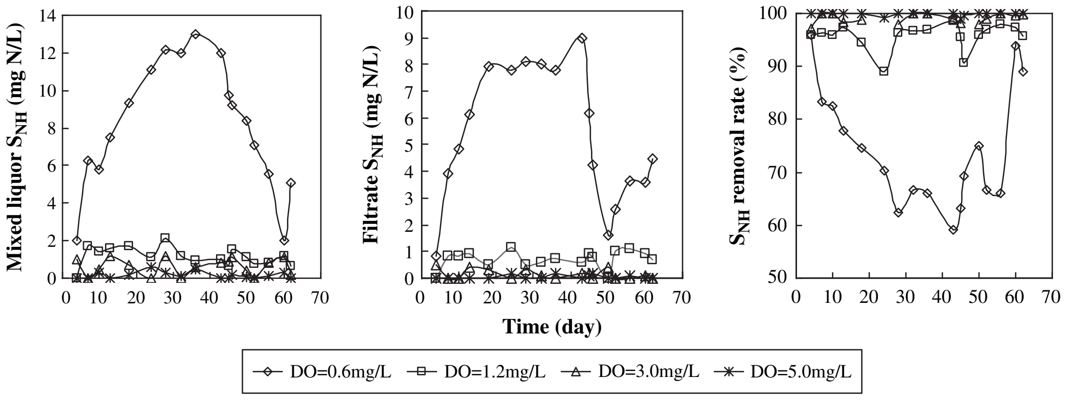

Fig. 3. S_{NH} removal at different DO concentrations.

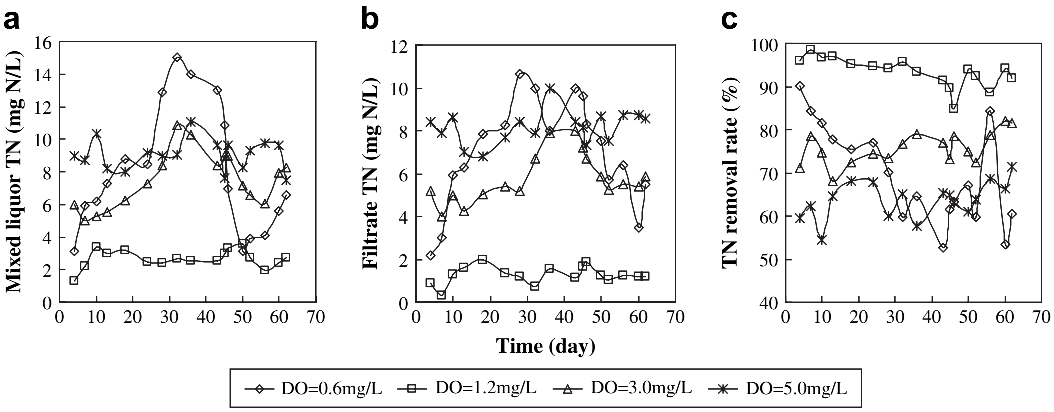

Fig. 4. Soluble TN removal at different DO concentrations.

reactor and effluent at the DO concentrations of 0.6 and 1.2 mg/L. It is easy to understand this observation since overall TN removal is related to both nitrification and denitrification processes. These results indicated that SND might occur in the SMBR system, dependently on the DO level. It is concluded that nitrification decreased, but denitrification increased with the decrease of DO concentration. This finding is well in agreement with the previous studies (Collivignarelli and Bertanza, 1999; Kazuaki et al., 2003). The optimal DO concentration favoring the TN removal was found to be 1.2 mg/L in the present study. The present results are quite consistent with other SMBR studies reporting optimal DO level for the SND (Holakoo et al., 2007). In a SMBR treating synthetic municipal wastewater, Holakoo et al. (2007) reported that ammonia and TN removals were improved as the operating DO was controlled in a range of 1–2 mg/L compared to other DO levels; nitrification was improved but denitrification deteriorated at a high DO of 2–3 mg/L, while nitrification has hampered due to oxygen limitation when the DO in the reactor decreased to 0.5 mg/L.

To remove nitrogen from wastewater, an aerobic nitrification followed by anaerobic denitrification is commonly used. The different requirement of nitrifiers and denitrifiers results in the necessity of keeping the processes separate, either in two reactors or in alternating aerobic and anaerobic zones. Previous studies revealed that these two important steps termed SND can occur concurrently in a single reactor (Watanabe et al., 1995; Chu et al., 2005; Chu et al., 2006). In a single reactor with continuous aeration, the SND were first noted in the biofilm and granule processes (Helmer and Kunst, 1998; Watanabe et al., 1995). Recent studies indicated that the SND might occur in the continuous aeration membrane bioreactor processes (Chu et al., 2005; Sun et al., 2007; Holakoo et al., 2007).

In a single reactor with continuous aeration, it is generally recognized that the SND occur as a consequence of DO concentration gradient distribution within microbial flocs, granules or biofilms due to diffusion limitation (Zhang et al., 1999; Chu et al., 2006; Holakoo et al., 2007). According to microenvironment theory, oxygen may be depleted at significant rates within the granules so that the DO cannot penetrate the entire depth of flocs, granules or biofilms. That is, nitrifiers will preferentially be active on the surface of the flocs, granules or biofilms, whereas the anoxic micro-zones in the center of flocs, granules or biofilms allow heterotrophic denitrifiers to produce nitrogen gas. It is postulated that a similar mechanism functions in the SMBR system: as ambient DO concentration was controlled in a certain range, forming an anoxic micro-zone inside the flocs allowed the denitrification. In the present study, TN removal was significantly limited as the DO concentration was higher than 3 mg/L, presumably due to the absence of anoxic environment. In fact, Silva et al. (1998) reported that the factors affecting SND were primarily ambient DO concentration and flocs size. Under low DO, diffusion limitations may create an anoxic zone within the biological flocs where denitrification can take place (Pochanna et al., 1999).

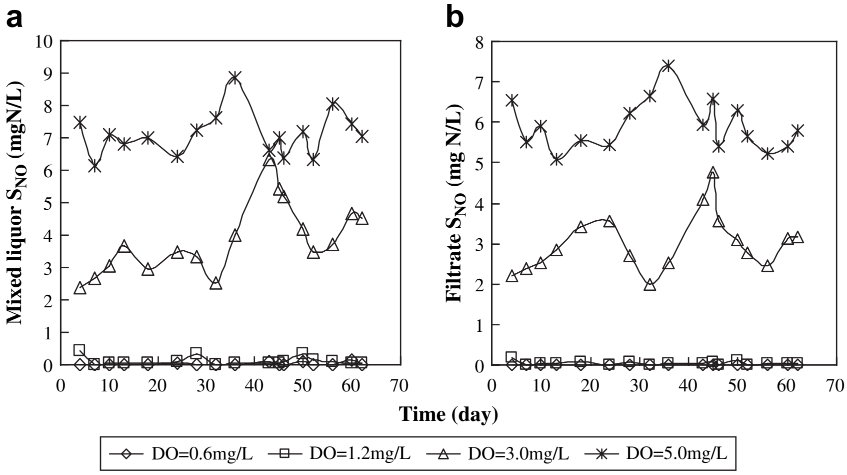

Fig. 5. Changes of S_{NO} at different DO concentrations over time.

Table 1
Components of TCM wastewater

Component	Definition	Value (mg/L)
S_{ND}	Soluble organic nitrogen	18.58
S_I	Soluble inert organic substrate	53.8
S_S	Readily biodegradable organic substrate	141.2
S_{NH}	Ammonium and ammonia nitrogen	20.52
S_{NO}	Nitrate and nitrite nitrogen	0.5
S_O	Dissolved oxygen	0
X_{ND}	Particulate readily biodegradable organic nitrogen	278.1
X_I	Particulate inert organic substrate	85.3
X_S	Slowly biodegradable organic substrate	2113.2
X_P	Particulate substances produced by biomass attenuation	0
$X_{B,H}$	Other-cultivate activated biomass	0
$X_{B,A}$	Self-cultivate activated biomass	0

Effective separation by the membrane is an important factor for the process (Mansell and Schroeder, 1999). As observed in Fig. 2, there was a significant difference in COD_{mix} (70–140 mg/l) and COD_{fit} (10–50 mg/L) at the tested DO levels. However, no or less differences could be found in the mixed liquor S_{NH}, S_{NO} and TN and filtrate S_{NH}, S_{NO} and TN (Figs. 3–5). This is probably attributed to the fact that S_{NH}, S_{NO} and TN might easily pass through the membrane. In contrast to the simple structure of inorganic nitrogen, raw TCM wastewater contains a series of complex compounds such as colophony, mucilage, alkaloid, terpene and hydroxybenzene. Some soluble macromolecular components might survive from the anaerobic digestion. In addition, digested TCM effluent might contain some soluble microbial products (SMPs) which had been known having polymeric structure. These macromolecular components, residues and SMPs could be easily intercepted and captured by the membrane. This suggests that SMBR process is the technology of choice for the treatment of digested TCM effluent compared to other biological processes.

3.3. Simulation model of simultaneous COD and nitrogen removal

Activated sludge model (ASM1) was developed to model biological treatment for organic carbon removal, nitrification, and denitrification (Henze et al., 1987a,b). The model was proposed by the International Association on Water Pollution Research and Control, later known as the International Association on Water Quality and now the International Water Association (IWA), and can be used to predict oxygen demand and sludge production in an activated sludge system. Two main concepts have been incorporated into the model. The first concept is that biodegradable COD in wastewater is composed of readily biodegradable COD and slowly biodegradable COD. The second concept in this model is death-regeneration. When the biomass decays, a portion of the decayed cell material is non-biodegradable and remains inert. The rest of the decayed material is slowly biodegradable and can be broken down to be used by active organisms for growth. The basic structure of ASM1 is a mass balance equation to describe the accumulation rate of a particular component within the system: accumulation = input − output + reaction.

Thirteen components are incorporated in model ASM1, and a mass balance equation can be derived for each of these components from the eight rate processes listed as follows: aerobic growth of active heterotrophic biomass ($X_{B,H}$); anoxic growth of $X_{B,H}$; aerobic growth of $X_{B,A}$; decay of $X_{B,H}$; decay of active autotrophic biomass ($X_{B,A}$); ammonification of soluble biodegradable organic nitrogen (S_{ND}); hydrolysis of entrapped organics; hydrolysis of entrapped organic nitrogen.

The basic processes and structure used in model ASM1 were adapted to develop a model suitable for a SMBR system treating high-strength wastewater. The main novelties of the present model compared to model ASM1 are highlighted here. Firstly, digested TCM wastewater is targeted in the present model, which is apparently different with model ASM1 wastewaters with respect to wastewater composition and strength. Secondly, in a submerged membrane bioreactor system, S_{ND} and particulate biodegradable organic nitrogen (X_{ND}) might pass through the membrane module. In such being case, permeate coefficient (f_m) was introduced into the present model. Considering all reactions occurring under a neutral pH condition, alkalinity is excluded from the model. In addition, because particulate (suspended) inert organic matter (X_I) and soluble inert organic matter (S_I) are unable to be degraded biologically, reaction rates of X_I and S_I are equal to zero, that is, $dX_I/dt = 0$, and $dS_I/dt = 0$. For simplicity, other key features and assumptions are summarized as follows: (1) reaction temperature is kept at a consistent value of 20 °C; (2) reaction pH is close to seven and constant; (3) coefficients of process rate expressions and nitration are constant; (4) autotrophic conversion of ammonia nitrogen to nitrate nitrogen is considered to be a single-step process which undergoes under aerobic conditions; (5) nitrogen limitation

Table 2
Stoichiometric, kinetic and process parameters

Item	Parameter	Definition	Value	Unit	Reference
Stoichiometric parameters	Y_H	Heterotrophic yield coefficient from substrate	0.49	g COD/g COD	This work
	Y_A	Autotrophic yield coefficient	0.24	g COD/g N	(Henze et al., 1987a, 2000; Lu et al., 2001)
	f_P	Inert fraction of biomass leading to particulate products	0.08	Dimensionless	(Henze et al., 1987a, 2000; Lu et al., 2001)
	i_{XB}	Mass N/mass COD in biomass	0.086	g N/g COD	(Henze et al., 1987a, 2000; Lu et al., 2001)
	i_{XP}	Mass N/mass COD in products from biomass	0.06	g N/g COD	(Henze et al., 1987a, 2000; Lu et al., 2001)
Kinetic parameters	$\widehat{\mu}_H$	Maximum specific growth rate of substrate for heterotrophs	3.65	Day^{-1}	This work
	K_S	Substrate half-saturation coefficient for heterotrophic biomass	56.97	$g\ COD/m^3$	This work
	$K_{O,H}$	Oxygen half-saturation coefficient for heterotrophic biomass	0.20	$g\ O_2/m^3$	(Henze et al., 1987a, 2000; Lu et al., 2001)
	K_{NO}	Nitrate half-saturation coefficient for denitrifying heterotrophic biomass	0.50	$g\ NO_3\text{-}N/m^3$	(Henze et al., 1987a, 2000; Lu et al., 2001)
	b_H	Heterotrophic decay coefficient for formation of particulate	0.43	Day^{-1}	This work
	η_g	Correction factor for anoxic growth of heterotrophs	0.9	Dimensionless	This work
	η_h	Correction factor for anoxic hydrolysis	0.4	Dimensionless	This work
	k_h	Hydrolysis coefficient	3.0	g COD/(g COD·d)	(Henze et al., 1987a, 2000; Lu et al., 2001)
	K_X	Half-saturation coefficient for hydrolysis of particulate biodegradable substrate	0.03	g COD/g COD	(Henze et al., 1987a, 2000; Lu et al., 2001)
	$\widehat{\mu}_A$	Maximum specific growth rate for autotrophs	0.166	Day^{-1}	This work
	K_{NH}	Ammonia half-saturation coefficient for autotrophic biomass	1.0	$g\ NH_3\text{-}N/m^3$	(Henze et al., 1987a, 2000; Lu et al., 2001)
	$K_{O,A}$	Oxygen half-saturation coefficient for autotrophic biomass	0.4	$g\ O_2/m^3$	(Henze et al., 1987a, 2000; Lu et al., 2001)
	k_a	Ammonification coefficient	0.08	$m^3/(g\ COD \cdot day)$	(Henze et al., 1987a, 2000; Lu et al., 2001)
	b_A	Autotrophic decay coefficient for formation of particulate	0.1	Day^{-1}	(Henze et al., 1987a, 2000; Lu et al., 2001)
Process parameters	f_m	Permeating factor through membrane	0.7	Dimensionless	Silva et al. (1998)

Table 3
Mathematical model expressions of simultaneous organic carbon and nitrogen removal in the SMBR

Component	Rate expression
S_S	$\frac{dS_S}{dt} = 28.3 - 0.2004S_S + 7.45\left(\frac{S_S}{56.97+S_S}\right)\left[\left(\frac{0.18}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right) - \left(\frac{S_O}{0.2+S_O}\right)\right]X_{B,H} + 3\left(\frac{X_S}{0.03X_{B,H}+X_S}\right)\left[\left(\frac{S_O}{0.2+S_O}\right) - \left(\frac{0.08}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right)\right]X_{B,H}$
X_S	$\frac{dX_S}{dt} = 423.5 - 0.0004X_S + 0.92(0.43X_{B,H} + 0.1X_{B,A})$
$X_{B,H}$	$\frac{dX_{B,H}}{dt} = -0.0004X_{B,H} + 3.65\left(\frac{S_S}{56.97+S_S}\right)\left[\left(\frac{0.18}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right) + \left(\frac{S_O}{0.2+S_O}\right)\right]X_{B,H} - 0.43X_{B,H} - 3\left(\frac{X_S}{0.03X_{B,H}+X_S}\right)\left[\left(\frac{S_O}{0.2+S_O}\right) + \left(\frac{0.08}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right)\right]X_{B,H}$
$X_{B,A}$	$\frac{dX_{B,A}}{dt} = -0.0004X_{B,A} + 0.166\left(\frac{S_{NH}}{1.0+S_{NH}}\right)\left(\frac{S_O}{0.4+S_O}\right)X_{B,A} - 0.1X_{B,A}$
X_P	$\frac{dX_P}{dt} = -0.1404X_P + 0.08(0.43X_{B,H} + 0.1X_{B,A})$
S_O	$\frac{dS_O}{dt} = 3.799\left(\frac{S_S}{56.97+S_S}\right)\left(\frac{S_O}{0.2+S_O}\right)X_{B,H} - 2.99\left(\frac{S_{NH}}{1.0+S_{NH}}\right)\left(\frac{S_O}{0.4+S_O}\right)X_{B,A}$
S_{NO}	$\frac{dS_{NO}}{dt} = 0.1002 - 0.2004S_{NO} - 1.195\left(\frac{S_S}{56.97+S_S}\right)\left(\frac{0.2}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right)X_{B,H} + 0.69\left(\frac{S_{NH}}{1.0+S_{NH}}\right)\left(\frac{S_O}{0.4+S_O}\right)X_{B,A}$
S_{NH}	$\frac{dS_{NH}}{dt} = 4.1125 - 0.2004S_{NH} - 0.3139\left(\frac{S_S}{56.97+S_S}\right)\left[\left(\frac{0.18}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right) + \left(\frac{S_O}{0.2+S_O}\right)\right]X_{B,H} - 0.7059\left(\frac{S_{NH}}{1.0+S_{NH}}\right)\left(\frac{S_O}{0.4+S_O}\right)X_{B,A} + 0.08S_{ND}X_{B,H}$
S_{ND}	$\frac{dS_{ND}}{dt} = 3.7237 - 0.1404S_{ND} - 0.08S_{ND}X_{B,H} + 3\left(\frac{X_{ND}}{0.03X_{B,H}+X_S}\right)\left[\left(\frac{S_O}{0.2+S_O}\right) + \left(\frac{0.08}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right)\right]X_{B,H}$
X_{ND}	$\frac{dX_{ND}}{dt} = 55.7356 - 0.0004X_{ND} - 0.0908(0.43X_{B,H} + 0.1X_{B,A}) - 3\left(\frac{X_{ND}}{0.03X_{B,H}+X_S}\right)\left[\left(\frac{S_O}{0.2+S_O}\right) + \left(\frac{0.08}{0.2+S_O}\right)\left(\frac{S_{NO}}{0.5+S_{NO}}\right)\right]X_{B,H}$

on organic substrate removal and cell growth is not specifically considered; (6) particulate organic substrates are caught by microorganism instantaneously; (7) hydrolyzation of organic substrate and nitrogen simultaneously occurs in an equal reaction rate.

As per the concepts used in ASM1 (Henze et al., 1987a), organic components of the TCM wastewater can be subdivided into a number of categories. Twelve components of TCM wastewater are given in Table 1. The values of kinetic and stoichiometric parameters of the model were derived either from the present pilot-scale study or from the literature (Henze et al., 1987a, 2000; Lu et al., 2001) (Table 2).

Based on the above analysis and assumptions, an SMBR model formulation containing 10 first-order linear differential equations was derived after integrating wastewater characteristics and reaction coefficients (Table 3).

3.4. *Validity of simulation model prediction*

The mathematical model developed in this study was a set of correlative differential equations. Command ode45 in MATLAB symbol toolbox was used to evaluate numerical solution of differential equation groups. Command ode45 is based on Runge–Kutta formula technique and is calculated by a single-step principium. The simulation program was compiled by MATLAB and derived initial values for TCM wastewater treatment in the SMBR are shown in Table 4. The simulated initial values are quite reasonable and comparable to those obtained by the IAW model (Henze et al., 1987a,b). This indicates that the MATLAB program is able to be applicable to the SMBR model.

To examine the effectiveness of the model, three SMBRs were aerated at a fixed air flow rate, but operated at HRTs of 8 h (SMBR1), 5 h (SMBR2) and 3.2 h (SMBR3), respectively. Shorter HRT favored the accumulation of biomass, but resulted in a lower level of DO concentration in reactor (data not shown). As the reactors reached steady-state conditions indicated by stable removals of COD, NH_4-N, and TN, and consistent retention of MLSS and MLVSS, samples were taken from the reactors and analyzed. The measured and simulated results are given in Table 5. Overall, the model well fitted

Table 4
Comparison of simulation initial values with one of IAW

Components	Initial values of the present program (mg/L)	Initial values of IAW (mg/L)
S_I	40.06	40
S_S	2.71	2.62
X_I	899.75	888.89
X_S	25.79	29.46
$X_{B,H}$	1444.19	1450.31
$X_{B,A}$	90.12	90.39
X_P	747.74	737.08
S_{NO}	30.60	33.31
S_{NH}	0.79	0.41
S_{ND}	0.90	0.93
X_{ND}	2.32	2.54

Table 5
Comparisons of the stimulated results with steady-state experimental data

Components	SMBR1		SMBR2		SMBR3	
	Measured value (mg/L)	Simulated value (mg/L)	Measured value (mg/L)	Simulated value (mg/L)	Measured value (mg/L)	Simulated value (mg/L)
S_I	55.7	54.12	53.8	53.87	53.4	53.8
S_S	35.8	36.46	42.6	40.08	42.7	43.72
X_I	831.4	859.08	1699.7	1683.72	2125.6	2139.77
X_S	82.7	80.28	60.9	58.77	36.4	37.25
$X_{B,H}$	6000	6075.72	10363.3	9972.64	15354.7	15498.55
$X_{B,A}$	–[a]	93.42	–	95.33	–	95.33
X_P	–	737.08	–	686.04	–	689.02
S_{NO}	20.15	20.74	14.3	14.48	10.2	10. 07
S_{NH}	0.8	0.75	1.0	0.99	10.4	10.58
S_{ND}	–	2.28	–	3.47	–	4.30
X_{ND}	–	3.01	–	5.4	–	7.04

[a] Not measured experimentally.

the laboratory data, regardless of COD or nitrogen conversion. In addition, same experimental trends of COD and nitrogen conversion with the DO level were indicated by the model. For example, with a decrease in DO, nitrate and nitrite nitrogen (S_{NO}) decreased, but ammonium and ammonia nitrogen (S_{NH}) increased. These findings indicate that the model is able to reflect and thus manage the operation of SMBR treating TCM wastewater. It needs to be pointed out that the above SMBR model was obtained from specific experiment substrate. Its applicability for more general situations remains to be examined.

4. Conclusions

Pilot-scale SMBRs were operated at different DO levels for the removal of organic substances and nitrogen of the digested TCM wastewater. Experimental results indicated that DO had an important effect on the removal of COD and the conversion of S_{NH}, S_{NO} and TN. Simultaneous nitrification and denitrification were able to be accomplished in the continuous-aeration SMBRs by controlling ambient DO concentration. It is postulated that, because of the oxygen diffusion limitation, an anoxic micro-zone was formed inside the flocs where the denitrification occurred. From four tested DO levels, the optimal DO concentration favoring COD and TN removal was found to be 1.2 mg/L. At that DO level, more than 96% COD and 90% TN were degraded.

A model was developed for the SMBR process of degrading the digested TCM effluent, taking into account the biological degradation and membrane separation. The model well fitted the laboratory data, and was able to simulate the removal of COD and nitrogen. It is suggested that the model proposed could reflect and manage the operation of SMBR treating a certain kind of industrial wastewaters.

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